

The competitive adsorption of fuel-type compounds on zeolite 13X

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Introduction

The possibility of selectively removing the nitrogenous components of fuels by adsorption on zeolite 13X was recently reported (1-2). The purpose of this work is to develop an industrial process to remove heteroatom components from synthetic crude fractions in order to decrease the need for hydrotreating or reduce the required severity of hydrotreating. The emphasis has been given to nitrogenous compounds since they dictate the severity of the process. Two of the most important criteria determining the success of an adsorption process are the adsorption capacity and the degree of selectivity. As found in the first two studies using a model solution there is a large degree of discrimination between nitrogenous compounds; the extent of adsorption is inversely proportional to the size and the acidity of the compound. The overall adsorption capacity obtained with the model solution is 10%. However, when using a real naphtha the capacity obtained is much smaller, being of the order of 1-3%. One of the potential reasons for this lower capacity could be the competitive adsorption of non-nitrogenous compounds contained in the naphthas.

The present study was undertaken to investigate the degree of competition between nitrogenous compounds and other compounds mainly olefins and oxygenated compounds. Very little competition from non-nitrogenous compounds was observed. Olefins were able to compete with nitrogenous compounds only at very high concentrations.

Experimental

All experiments were performed at room temperature in a continuous-flow fixed-bed adsorption apparatus. The zeolite is dry-packed in a stainless steel column 20 cm long and 0.4 cm ID. The first series of tests were done with a zeolite dried at 160 °C. The feed is pumped at a constant flow of 0.5 mL/min and samples of the effluent are collected every 5 mL and subsequently analyzed by gas chromatography.

The adsorption capacity of individual compounds was obtained using a 1 wt% solution in toluene of the desired compound. For the competitive runs a solution of 1 wt% of each compound in toluene (2 wt% total) was used.

Results and discussion

Several factors affect the magnitude of adsorption; the adsorption capacity depends on the operating conditions such as inlet concentration, bed depth, flow rate and most importantly the affinity of the sorbate for the surface. For a given set of operating conditions the capacity measures the relative affinity of the sorbate for the solid and the solution. In the first part of this study the effect of the nature of the solution on the adsorption of aniline is investigated (Table 1). The maximum capacity is obtained for a toluene solution; the extent of aniline adsorption decreases following the addition of heptane, cyclohexene and indene. It should be noted that the degree of reproducibility between packings gives an error of 10-15%. Thus the results indicate that an olefinic solution might interfere with the adsorption of the nitrogenous compounds. This could explain the results recently reported showing a large difference in adsorption capacities for two naphthas; the lowest capacity was obtained for a naphtha abnormally high in olefins (Ref. 1, Table 2; adsorption capacity of 1 wt% for the naphtha containing 62% olefins).

Table 2 presents a summary of the adsorption capacities of various compounds. The extent of adsorption seems to be proportional to the polarity and the basicity of the compound. The indene-indoline-indole series illustrates this point; the capacities for these compounds are 3.99, 13.7 and 14.81 wt% respectively. At a concentration of 1 wt%, the olefins have very little affinity

for the zeolite as indicated by their low capacities; they do interfere with the adsorption of aniline as shown in Table 3. Oxygenated compounds have a strong affinity for the zeolite. The extent of adsorption of phenol compares to those of aniline and indole, two of the most retained nitrogenous compounds. Under competition, phenol is quite successful in displacing the nitrogenous compounds (Table 4). These results suggest that naphthas high in oxygenated compounds could be treated using the adsorption process. This could be advantageous for synthetic crude naphthas such as coal derived liquids.

The study on competition between nitrogenous compounds show that the adsorption capacity of individual compounds is a good predictor of the adsorption process for a complex mixture. Indeed the order of affinity indicated by the adsorption capacity of the individual compound is very similar to the order obtained for a solution containing eighteen compounds (1). Except for a few cases the individual capacities also predicted the relative capacities for the "two compound competitions" showed in Tables 3-7. The results indicate that the total capacity obtained is of the order of 15 wt%. The adsorption is not dominated by a single nitrogenous compound.

Conclusion

The data obtained in this study show that there should be little competition from non-heteroatom compounds except possibly from olefins. Both nitrogenous and oxygenated compounds have a strong affinity for the zeolite. The adsorption of oxygenated compounds presents a real advantage since these compounds are also problematic. Oxygenated compounds are present in significant amounts in a variety of synthetic crude fractions.

An adsorption process for the removal of heteroatom components, using a zeolite 13X, would not be efficient because of the low affinity of a number of nitrogenous compounds. For instance phenylpiperidine and collidine are adsorbed at less than 8 wt% without any competition (Table 2). This capacity will decrease in a multi-component solution because of site competition. Future work should concentrate of finding an adsorbent that can remove the less basic compounds.

- 1) G. Jean, S. Ahmed and H. Sawatzky, "The Selective Removal of Nitrogenous-Type Compounds from Fuels by using zeolites", Sep. Sci. Technol. 20(7 & 8), 555-564, 1985
- 2) G. Jean, E. Bonvie and H. Sawatzky, "Selective Removal of Nitrogenous Compounds Using Zeolites", ACS National Meeting Chicago Sep. 8-13: Preprint Fuel Division Vol. 30(4), 474-480, 1985

Table 1

Solvent effect on aniline adsorption capacity (wt% on zeolite)
1 wt% aniline in solvent

Solvent	Capacity %	Capacity relative to toluene
toluene	22.91	—
50:50 toluene/heptane	19.28	0.84
50:50 cyclohexene	15.13	0.66
50:50 1-indene	15.09	0.65

Table 2

Adsorption capacity for individual compounds (wt% on zeolite)
1 wt% in toluene

Compound	Capacity %	Compound	Capacity
Decene	1.21	Cycloheptanone	11.70
Indene	3.99	Octylamine	11.91
1-Phenethylpiperidine	5.73	Dibenzylamine	12.99
Aminoanthracene	5.98	Indoline	13.70
2,4,6-Collidine	7.24	4-Ethylpyridine	14.01
1,2,5-Trimethylpyrrole	8.47	Quinoline	14.45
2-Phenylpyridine	8.69	Iso-Quinoline	14.72
Phenothiazine	9.04	Indole	14.81
2,2'-Dipyridyl	10.45	Phenol	16.08
Decylalcohol	11.18	Aniline	22.91

Table 3

Adsorption capacity for various compounds in the presence of Aniline (wt% on zeolite)
1 wt% compound and 1 wt% aniline in toluene

Compound	Capacity %	Relative Capacity	Aniline capacity %	Aniline Relative Capacity	Total Capacity
Decene	0.43	0.36	16.21	0.74	16.63
Indene	1.07	0.28	13.64	0.59	14.71
Dibenzylamine	3.66	0.28	15.38	0.67	19.04
Decylalcohol	5.43	0.49	15.16	0.66	20.59
Indole	7.39	0.50	12.66	0.55	20.05
2,2'-Dipyridyl	7.77	0.74	7.67	0.34	15.44
Quinoline	8.92	0.62	11.79	0.52	21.71
Indoline	9.86	0.72	16.82	0.74	26.68

Table 4

Adsorption capacities for various compounds in the presence of Phenol (wt% on zeolite)
1 wt% compound and 1 wt% phenol in toluene

Compound	Capacity %	Relative Capacity	Phenol capacity %	Phenol Relative Capacity	Total Capacity
Dibenzylamine	3.57	0.28	10.59	0.66	14.11
Quinoline	4.75	0.44	11.80	0.73	16.55
2,2'-Dipyridyl	5.71	0.55	9.06	0.56	14.77
Indole	7.61	0.51	13.27	0.83	20.88
Decylalcohol	7.68	0.69	11.41	0.71	19.09

Table 5

Adsorption capacities for various compounds in the presence of Octylamine (wt% on zeolite)
1 wt% compound and 1 wt% octylamine in toluene

Compound	Capacity %	Relative Capacity	Octylamine capacity %	Octylamine Relative Capacity	Total Capacity
2,2'-dipyridyl	8.21	0.79	6.62	0.56	14.83
4-Ethylpyridine	8.59	0.77	4.41	0.37	13.00
Dibenzylamine	8.91	0.69	6.98	0.59	15.89
Cycloheptanone	9.40	0.80	5.68	0.48	15.08
Quinoline	9.70	0.90	6.89	0.56	16.59
Indole	10.06	0.68	6.76	0.62	16.82

Table 6

Adsorption capacities for various compounds in the presence of 4-Ethylpyridine (wt% on zeolite)
1 wt% compound and 1 wt% 4-ethylpyridine in toluene

Compound	Capacity %	Relative Capacity	4-Ethylpyridine capacity %	4-Ethylpyridine Relative Capacity	Total Capacity
Quinoline	5.65	0.52	5.59	0.50	11.24
Decylalcohol	5.74	0.51	9.45	0.85	15.19
Dibenzylamine	5.79	0.45	9.06	0.82	14.85
Indoline	6.19	0.45	7.29	0.66	13.48
Indole	7.13	0.48	6.82	0.61	13.95
Cycloheptanone	7.90	0.68	9.53	0.86	17.43
2',2''-Dipyridyl	8.34	0.80	5.89	0.53	14.23
Aniline	13.97	0.61	8.32	0.75	22.29

Table 7

Adsorption capacities for various compounds in the presence of Quinoline (wt% on zeolite)
1 wt% compound and 1 wt% quinoline in toluene

Compound	Capacity %	Relative Capacity	Quinoline capacity %	Quinoline Relative Capacity	Total Capacity
Decylalcohol	1.78	0.16	9.35	0.87	11.13
Dibenzylamine	4.23	0.33	9.46	0.88	13.69
2-Phenylpyridine	5.21	0.60	9.14	0.85	14.35
Indole	5.85	0.40	7.11	0.65	12.96
Indoline	7.23	0.53	8.63	0.80	15.86
2,2''-Dipyridyl	8.05	0.77	4.37	0.40	12.42
Aniline	11.19	0.52	8.92	0.62	20.11